

SOAP OPERA: POLYMER-SURFACTANT INTERACTIONS ON THIN FILM SURFACES

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ABSTRACT

Surfactants are macromolecules with unique properties. They commonly contain a polar head group with a nonpolar hydrocarbon chain. These properties allow surfactants to solubilize greases and other nonpolar molecules. One particular way that this is accomplished is through the formation of micelles. Micelles are formed at the critical micelle concentration (cmc), which varies depending upon the nature of the surfactant and also the media in which the surfactant resides. These micelles can take a variety of shapes, but are generally characterized by surrounding the grease with the nonpolar hydrocarbon chains, exposing only the polarized head groups to the media, usually water. This property of easy solubilization has made surfactants a very attractive industrial agent. They are used most conventionally as industrial cleaning agents and detergents. However, they also have lesser-known applications in conjunction with polymers and other macromolecular mixtures, often creating a system with novel properties, such as increased solubilization and smoother mixture consistency.

A recently developed field has investigated the self-assembly of polymers and polyelectrolytes onto thin film surfaces. There are many reasons for studying this process, such as for second harmonic generation purposes and bioassays.

In this study, the interaction between the anionic polyelectrolyte poly[1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO) and two surfactants of opposite charge, Sodium Dodecyl Sulfate (SDS) and Dodecyl Trimethyl Ammonium Bromide (DTAB), in their assembly onto thin film surfaces was investigated. The kinetics of adsorbance onto the thin films was examined, followed by construction of 10-bilayer films using an alternating layer of the cationic polyelectrolyte poly(ethylenimine) (PEI) to provide the electrostatic means for the PAZO/surfactant combination to assemble onto the thin film. The kinetics of adsorption is being characterized primarily with UV-visible spectroscopy, whereas the ten bilayers are being studied with both UV-visible spectroscopy and ellipsometry.

Preliminary results suggest that the rate of adsorbance of various concentrations of SDS below and above the cmc in PAZO is not significantly different from the rate of adsorbance of pure PAZO. However, the amount of adsorbed material decreases as the concentration of SDS dissolved into PAZO increases. This has allowed for less PAZO adsorbance to be detected in the 10-bilayer systems.



Preliminary kinetics data suggest longer saturation times for DTAB/PAZO systems, but amount adsorbed may be increased from pure PAZO systems. Further work is being conducted on the kinetics, and more 10 bilayer films remain to be built and characterized. *In situ* methods of studying the films will also be examined in the future.

INTRODUCTION

Surfactants (a condensation of surface active agents) have long been a subject of interest for both academic and industrial purposes. Their properties have been utilized for a number of different purposes, including hair and skin care products, detergency, and oil recovery. There has been a recent move to mix polymers, especially neutral polymers or oppositely charged polyelectrolytes, with surfactants, usually to take advantage of their individual properties, but also sometimes to obtain a unique property that occurs in their combination. One example of this is in the hair care industry, where the addition of the polymer reduces the effective surfactant monomer concentration, thereby making the soap less harsh [1].

The authors are examining polymer-surfactant interactions on thin film surfaces. The film is built using self-assembly dipping procedures [2] onto glass or silicon wafers. Reasons for studying thin-film polymer-surfactant interactions include possible polymer alignment abilities for second harmonic generation [3], biosensors, and drug delivery systems.

The cationic polyelectrolyte used is poly(ethylenimine) (PEI), which was chosen for its small monomer unit and its commercial availability. The anionic polyelectrolyte used is Poly[1-[4-(3-carboxy-4hydroxy-phenylazo)benzene sulfonamido]-1,2-ethanediyl, sodium salt] (PAZO), chosen for its commercial availability and its chromophore, which is very easily detected using UV-Visible Spectroscopy. The cationic surfactant dodecyl trimethyl ammonium bromide (DTAB) and the anionic surfactant sodium dodecylsulfate (SDS) were both used in combination with PAZO to study the effect of cooperative and competitive effects, respectively, on the adsorption of PAZO to the thin film surface. A number of techniques are available for the study of polymer-surfactant interactions [4], for isolated surfactant systems [5], and for surface interactions [6]. In this study, multilayer films were characterized using single wavelength ellipsometry, UV-Visible spectrometry, and atomic force microscopy (AFM). Bulk solution properties were examined using surface tensiometry.

METHODS

Solution Preparation

Solutions were prepared using the monomer molecular weight to calculate various millimolar concentrations. All solutions were prepared with ≥ 18 M Ω /cm nanopure water. The polyelectrolytes were examined in 1mM concentrations, while surfactant concentrations were examined roughly in set fractions above and below the surfactants' published cmc's in pure water. All chemicals were obtained from Sigma-Aldrich.

Piranha Etch

Glass and silicon substrates were treated for one hour at $\geq 80^\circ$ C in a 100 ml solution of 3 parts hydrogen peroxide, 30% weight, and 7 parts sulfuric acid, obtained from Fisher

Scientific. Rinsed several times afterwards with nanopure water and sonicated in nanopure water for 15 minutes.

Self-Assembly Procedure

Piranha etched substrates were dipped in 25 ml of polymer solution for set amounts of time, depending on nature of polymer and study. After each interval, the substrate was removed, rinsed in four separate beakers of nanopure water for 2 seconds each, and then dried under a dry nitrogen source for data analysis preparation.

RESULTS

Critical Micelle Concentration in Bulk Solution

The cmc for SDS in pure water is in good agreement with what is reported in the literature, lying at approximately 8mM. This author finds the cmc for SDS in 1mM PAZO to be only very slightly lower from that in pure water, despite competitive effects. On the other hand, surface tension immediately drops in solutions of 1mM PEI and SDS, making a clear cmc is difficult to determine. Data under 1mM concentrations of SDS in PEI solution are unreliable since the solution becomes cloudy at lower concentrations.

Kinetics

The kinetics of SDS is very straightforward (see Fig. 1). Saturation times seem to occur uniformly at five minutes, regardless of surfactant concentration. However, the higher SDS concentration leads to overall less PAZO adsorption to the surface.

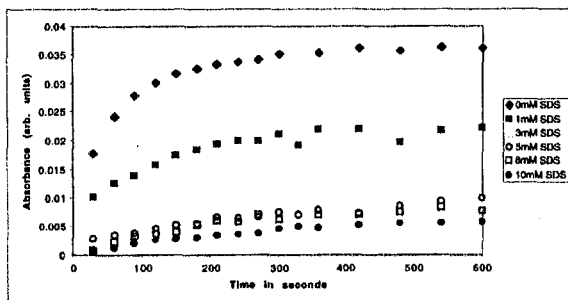


Figure 1: SDS Kinetics Data

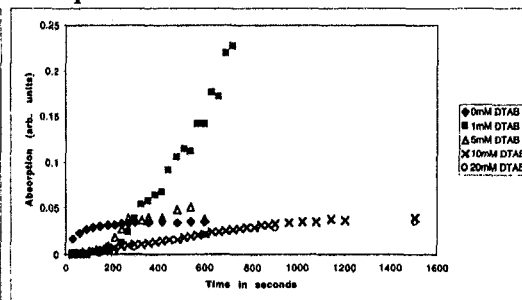


Figure 2: DTAB Kinetics Data

The DTAB kinetics is not easily interpreted. However, there are some notable features that should be mentioned (Fig. 2). First, the growth curve seems to be more sigmoidal than its SDS counterpart. The saturation time also appears to be longer than for SDS (approximately 40 minutes in the higher concentrations), but this time may hold regardless of DTAB concentration. Also, the total adsorption appears to be higher than pure PAZO adsorption but, like its anionic counterpart, the total adsorption does decrease with increasing surfactant concentration.

10-bilayer formation

SDS multilayer thin films are fairly easily characterized. The bilayer PAZO absorptions (Fig. 3) and thicknesses (Fig. 4) indicate two general trends in the growth: (a) the growth is linear, and (b) the slope for the bilayer growth tends to decrease as the surfactant concentration increases. These conclusions are not unexpected, given the results of the kinetics experiments above.

The DTAB multilayer thin film results are still very incomplete. Preliminary ellipsometry data does not elucidate any trend in building, other than a severe reduction

in total thickness from the pure PAZO system. Similarly, the UV absorption shows a decrease in the total amount of PAZO adsorbed. However, it is interesting to note that the growth resembles the kinetics growth and that the total absorption from one bilayer in the kinetics work is higher than 10 bilayers at longer dipping intervals (data not shown).

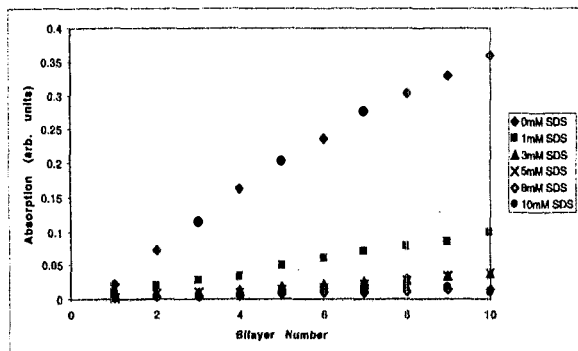


Figure 3: Bilayer absorption peaks for SDS in PAZO

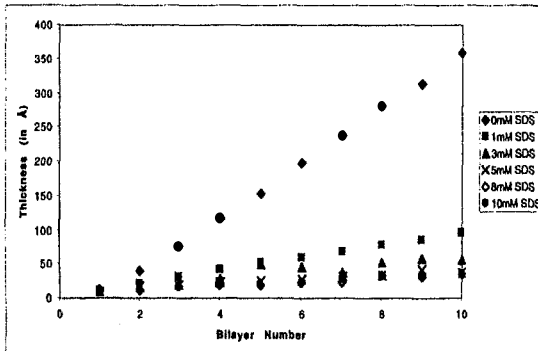


Figure 4: Bilayer thickness peaks for SDS in PAZO

Atomic Force Microscopy

A 10-bilayer film of pure PEI and PAZO on a glass slide was examined using AFM. As seen in Fig. 5, the surface is very uniform, with a root mean square roughness of only 5.29 nm.

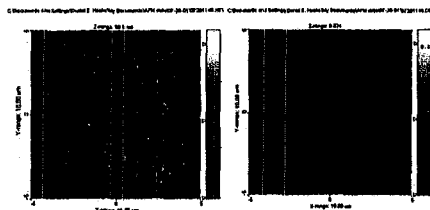


Figure 5: Atomic Force Microscopy data of a 10-bilayer PEI/PAZO film yields uniform surface results.

DISCUSSION

The SDS/PAZO system has begun to be characterized. Bulk surface tension measurements indicate that the cmc does not depreciate by much. However, despite the presence of micelles in the bulk dipping solution in the 8mM and 10mM concentrations, PAZO adsorption still tends to decrease, and saturation times seem to remain the same. Though PAZO adsorption to a surface is thermodynamically favored due to its large size, the comparably much smaller and more abundant SDS monomers (and possibly micelles) still outcompete the polymer very significantly, decreasing total PAZO adsorption by orders of magnitude with only several millimolar increases in surfactant concentration. This is probably due to the very strong interactions that occur between PEI and SDS. Competition is very reproducible, producing very linear fits in 10-bilayer film growths, both in thickness and in UV absorbance.

The DTAB results are still very much incomplete and are not easily interpreted. Complications from the heterogeneity of the mixture may contribute to this problem since solutions are turbid for every solution above 1mM and, in fact, surfactant deposits can be seen on the substrates at low DTAB concentrations. It will certainly be interesting to see how much the cmc changes from the reported value of 15.1mM when introduced into PAZO, and whether this will have an effect on the subsequent thin film building. DTAB

ellipsometry data is also very hard to interpret, but this may be a result of the heterogeneous solutions or possibly erroneous assumptions made in ellipsometry thickness calculations. It is also certainly curious to see similarly shaped growth curves in the 10-bilayer film and its kinetics counterpart, not to mention that the total UV absorbance for the 10-bilayer film, though dipped in solution for far longer than the one layer in the kinetics study, was significantly less. There may be a number of reasons for this, such as possible mechanical contributions from the action of dipping, water molecule incorporations, or the temporary air interface created during measurements. This most certainly must be explored in more detail.

CONCLUSION

Much work remains to be done in this area. In addition to performing further *ex situ* studies of DTAB/PAZO systems, doing *in situ* measurements of all of the systems may prove beneficial in the removal of variables from the study, such as the effect of nitrogen drying and the air interface. Furthermore, it would be interesting to examine the effects of a neutral surfactant in PAZO solution as a comparison to its anionic and cationic extremes. Additional AFM data could prove interesting to compare surface roughnesses of varying surfactant concentrations in polymer solution. Finally, fluorescently probing micelles would be one last item of interest to determine the micellar composition of the adsorbed polymer-surfactant layers.

Though much work remains to be done, a preliminary understanding of this very recent field of polymer-surfactant interactions on thin film surfaces has been achieved.

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